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SEMICLASSICAL MOLECULAR DYNAMICS OF WAVEPACKETS IN  
ONE-DIMENSIONAL PHASE (U) STATE UNIV OF NEW YORK AT  
BUFFALO DEPT OF CHEMISTRY A HAGUE ET AL. JUL 87

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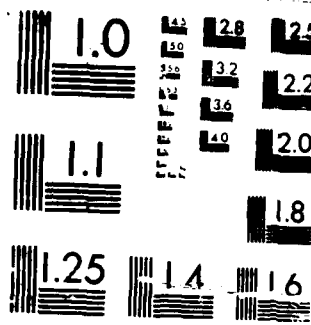
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Contract N00014-86-0043

TECHNICAL REPORT No. 47

Semiclassical Molecular Dynamics of Wavepackets in One-Dimensional  
Phase Space

by

Azizul Haque and Thomas F. George

Prepared for Publication

in

Condensed Matter Theories, Volume 3  
Edited by J. Arponen, R. F. Bishop and M. Manninen  
Plenum, London

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July 1987

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SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/87/TR-47			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260			7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043	
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217			10. SOURCE OF FUNDING NOS.		
			PROGRAM ELEMENT NO.		TASK NO.
			PROJECT NO.		WORK UNIT NO.
11. TITLE Semiclassical Molecular Dynamics of Wavepackets in One-Dimensional Phase Space					
12. PERSONAL AUTHOR(S) Azizul Haque and Thomas F. George					
13a. TYPE OF REPORT		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Yr., Mo., Day) July 1987	
				15. PAGE COUNT 17	
16. SUPPLEMENTARY NOTATION Prepared for publication in <u>Condensed Matter Theories</u> , Volume 3, edited by J. Arponen, R. F. Bishop and M. Manninen (Plenum, London)					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	SEMICLASSICAL, DENSITY MATRIX,		
			MOLECULAR DYNAMICS, NONLINEAR POTENTIALS,		
			WAVEPACKETS, MIXED STATES		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A semiclassical method for solving the quantum Liouville equation in one-dimensional phase-space is described. The development is based on constructing a Gaussian density matrix and is applicable to systems in pure and in mixed states having nonlinear interaction potentials. The density matrix is constructed using a set of dynamics variables whose expectation values are considered to be relevant for the dynamics. The self-consistent equations of motion are then derived for these expectations from the quantum Liouville equation using a projection scheme. The solution of these self-consistent equations provides the time evolution of the density matrix. The present method can yield, in principle, exact values for the expectations for all times. A model calculation is carried out to describe the vibrational motion of an arbitrary diatomic molecule on an anharmonic potential surface. However, the potentiality of this method lies in describing the time evolution of systems in mixed states and hence in describing the dynamics of molecular processes in condensed phases. (Keywords: )					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input checked="" type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson			22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

SEMICLASSICAL MOLECULAR DYNAMICS OF WAVEPACKETS IN ONE-DIMENSIONAL  
PHASE SPACE

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ABSTRACT

A semiclassical method for solving the quantum Liouville equation in one-dimensional phase-space is described. The development is based on constructing a Gaussian density matrix and is applicable to systems in pure and in mixed states having nonlinear interaction potentials. The density matrix is constructed using a set of dynamic variables whose expectation values are considered to be relevant for the dynamics. The self-consistent equations of motion are then derived for these expectations from the quantum Liouville equation using a projection scheme. The solution of these self-consistent equations provides the time evolution of the density matrix. The present method can yield, in principle, exact values for these expectations for all times. A model calculation is carried out to describe the vibrational motion of an arbitrary diatomic molecule on an anharmonic potential surface. However, the potentiality of this method lies in describing the time evolution of systems in mixed states and hence in describing the dynamics of molecular processes in condensed phases.

I. INTRODUCTION

Recent advances in the experimental study of the various molecular dynamical processes in condensed phase, such as energy transfer, molecular dissociation reactions, spectral line shapes, etc., require theoretical models for the quantitative understanding of the dynamical processes involved in condensed phases. There has been progress in studying equilibrium properties using classical [1], semiclassical [2], fully quantum mechanical [3] and quantum field theoretic methods [4,5]. Methods are also available for treating time-dependent processes within the classical framework [6]. However, very few theoretical developments are available for treating time-dependent processes incorporating quantum effects. These are the quantum corrections to the classically computed time-correlation functions [7], the exp(S) approach of Arponen and co-workers [4] and the semiclassical Gaussian wavepacket dynamics (GWD) approach developed notably by Heller [8]. The semiclassical GWD approach describes a self-consistent solution of the time-dependent Schrödinger equation and thus is restricted in its application to systems in pure states. Extension of this GWD method to the simulation of time-dependent properties of N-particle systems interacting through realistic pair potentials within the variational and nonvariational framework are also available in the literature [9]. Such application requires tedious thermal

averaging, which arises from the fact that we have no knowledge about initial conditions of the N-particle system.

Our objective is to develop a similar GWD approach which as such is applicable to systems in pure and in mixed states. That is, when treating systems in mixed states, we do not need to perform tedious thermal averaging. Our development satisfies the maximum entropy principle [10] when treating equilibrium or nonequilibrium systems. However, we do not make the assumption that the exact nonequilibrium statistical density matrix is approximately equal to the local equilibrium one [11-13]. For an N-particle statistical system it is practically impossible to construct a density matrix which contain all information about the system. However, with the advent of projection operator techniques [11,14], it has been possible to construct density matrices which contain information sufficient for the calculation of various physical quantities of interest.

In this paper we are interested in a reduced description of the exact N-particle system, which is the time evolution of the N single-particle density matrices in a mixed state. We define our reduced density matrix,  $\rho_{re}(X, X', t)$ , as a product of N single-particle density functions

$$\rho_{re}(X, X', t) = \prod_{j=1}^N \phi_j(x_j, x'_j; t) \quad , \quad (1)$$

where X is a vector with N coordinate components  $x_1 \dots x_N$ . The time evolution of these density functions,  $\phi_j$ , are then obtained from the quantum Liouville equation using a projection operator scheme [11,14]. We define each single-particle density function  $\phi_j(x_j, x'_j; t)$  from the perspective of nonequilibrium statistical mechanics as [10,11,14]

$$\begin{aligned} \phi_j(x_j, x'_j; t) &= \langle x_j | \hat{\phi}_j(t) | x'_j \rangle \\ &= \langle x_j | \exp \left[ \sum_{\alpha=0} \lambda_{j\alpha}(t) A_{j\alpha} \right] | x'_j \rangle \quad , \end{aligned} \quad (2)$$

which contains all information about the single particle system. The  $\lambda_{j\alpha}(t)$ 's are Lagrange multipliers, and the  $A_{j\alpha}$ 's are the dynamical variables. Since we are not interested in all the information contained in the  $\phi_j$ 's, we construct our  $\phi_j$ 's with respect to the six dynamical quantities

$$\begin{aligned} A_{j0} &= \hat{1}, \quad A_{j1} = \hat{x}_j, \quad A_{j2} = \hat{p}_j, \quad A_{j3} = \hat{x}_j^2, \\ A_{j4} &= \hat{p}_j^2, \quad A_{j5} = \hat{x}_j \hat{p}_j + \hat{p}_j \hat{x}_j \quad , \end{aligned} \quad (3)$$

where  $p_k$  is the momentum associated with the k-th particle and the hat designates an operator. As we shall see later, the choice of these dynamical quantities allows us to describe the time evolution of each single-particle density function incorporating quantum fluctuations. The time evolution of the expectations of these dynamical quantities,  $\langle A_{j\alpha} \rangle$ , are then obtained from the quantum Liouville equation using the projection operator scheme [11,14]. The choice of the single-particle density operator as given by Eq. (2) is by no means unique. Our choice is motivated by the physical consideration which is the maximum entropy principle [10,11].

We confine our development to one-dimensional phase space. In the next section we derive the equations of motion for the expectations,  $\langle A_{j\alpha} \rangle$ , in closed form and construct the corresponding density function for mixed states. In Sec. III we show that under certain conditions the density

function for mixed states reduces to the density function for pure states. To describe the time evolution of the pure state density function, we then derive the equations of motion for the corresponding dynamical quantities. In Sec. IV we show that our maximum entropy-based density function can also describe the time evolution of a harmonic system in thermal equilibrium [15]. In Sec. V we solve the equations of motion for the pure state to describe the vibrational motion of an arbitrary diatomic molecule on a Morse potential surface. We then compare our results with those obtained using the existing Gaussian wavepacket dynamics method [8,9], and a discussion is provided in Sec. VI.

## II. CONSTRUCTION OF THE DENSITY FUNCTION AND DERIVATION OF THE EQUATIONS OF MOTIONS FOR SYSTEMS IN MIXED STATES

We characterize our N-particle system by a Hamiltonian

$$H = \sum_{k=1}^N \frac{p_k^2}{2m_k} + V(x_1 \dots x_n) \quad (4)$$

and a density matrix  $\rho(X, X'; t)$  which satisfies the quantum Liouville equation

$$\frac{d\rho}{dt} = -iL\rho \equiv -(i/\hbar)[H, \rho] \quad (5)$$

where  $m_k$  is the mass of the k-th particle and  $V$  is the interaction potential. Since we are interested only in the time evolution of the N single-particle density functions, we partition our total density matrix as

$$\rho(t) = \rho_{re}(t) + \rho_{ir}(t) \quad (6)$$

where  $\rho_{re}(t)$  is a reduced description of the N-particle interacting system and is represented by a product of N single-particle density functions as described in Eq. (1).  $\rho_{ir}(t)$  represents the irrelevant degrees of freedom, since it does not contain any dynamical degrees of freedom of any single particle in the coupled N-particle system, but rather the correlations between single particle systems produced by their interaction.

We associate entropy  $S$  with our system by using the relation [10]

$$S = -k \text{Tr} \rho_{re}(t) \ln \rho_{re}(t) \quad (7)$$

where  $k$  is Boltzmann's constant. We maximize entropy subject to the constraints

$$\text{Tr} \rho_{re}(t) = 1 \quad (8a)$$

and

$$a_{ja}(t) = \langle A_{ja}(t) \rangle = \text{Tr} A_{ja} \rho_{re}(t) \equiv \text{Tr} A_{ja} \rho(t) \quad (8b)$$

where the  $A_{ja}$ 's are the 6N dynamical variables of interest to us.

We now derive explicit expressions for the time evolution of the expectations,  $a_{ja}(t)$ , using the time-dependent projection operator scheme [14] followed in constructing the maximum entropy distribution of the reduced density operator  $\rho_{re}(t)$  in one-dimensional phase space. From now on we shall refer to these equations of motion as reduced equations of motion since they describe the time evolution of the reduced density operator  $\rho_{re}(t)$ . We shall

use the projection operator technique in Liouville space [11,14]. In this space  $\hat{H}$  and  $\rho(t)$  can be written as  $|H\rangle\rangle$  and  $|\rho(t)\rangle\rangle$ . In this notation Eq. (8b) becomes

$$A_{j\alpha}(t) = \langle\langle \rho_{re}(t) | A_{j\alpha} \rangle\rangle \equiv \langle\langle \rho(t) | A_{j\alpha} \rangle\rangle . \quad (8c)$$

For each degree of freedom  $j$ , we now define a  $6 \times 6$  matrix with elements

$$D_{\alpha\beta}^j(t) = \langle\langle A_{j\alpha} | \rho_{re}(t) A_{j\beta} \rangle\rangle \equiv \text{Tr}[A_{j\alpha}^\dagger \rho_{re}(t) A_{j\beta}]$$

$$\alpha, \beta = 0, 1, \dots, 5 \quad (9)$$

and the Liouville space projection operator

$$P(t) = \sum_{j=1}^N \sum_{\alpha, \beta=0}^5 |\rho_{re}(t) A_{j\alpha}\rangle\rangle [D^j(t)]_{\alpha\beta}^{-1} \langle\langle A_{j\beta} | \quad (10)$$

having the following properties:

$$a) P(t) P(t') = P(t); \quad t > t' \\ P^2(t) = P(t) \quad (11a)$$

$$b) P(t) |\rho(t)\rangle\rangle = |\rho_{re}(t)\rangle\rangle \quad (11b)$$

$$c) \langle\langle A_{j\alpha} | P(t) \dot{\rho}(t) \rangle\rangle = \langle\langle A_{j\alpha} | \dot{\rho}_{re}(t) \rangle\rangle$$

$$\text{where } \dot{\rho}(t) = \frac{d\rho(t)}{dt} \text{ and } \dot{\rho}_{re}(t) = \frac{d\rho_{re}(t)}{dt} \quad (11c)$$

$$d) P(t) |\rho(t) A_{j\beta}\rangle\rangle = |\rho_{re}(t) A_{j\beta}\rangle\rangle . \quad (11d)$$

It has been shown in a separate communication [16] that the properties (11) can easily be derived using the definitions (9) and (10).  $P(t)$ , therefore, is the projection operator, since it reduces the exact density matrix  $\rho(t)$  to the simpler distribution  $\rho_{re}(t)$ .

Let us now assume that at some time  $t = t'$

$$\rho(t') = \rho_{re}(t') . \quad (12)$$

Using this assumption and introducing the complementary projection

$$Q(t) = 1 - P(t) \quad (13)$$

as shown in Ref. 16, we can write the exact reduced equations of motion (REM) for the  $a_{j\alpha}(t)$ 's from the quantum Liouville equation (5) as

$$\dot{a}_{j\alpha}(t) = -i \langle\langle A_{j\alpha} | L | \rho_{re}(t) \rangle\rangle + \sum_{\beta} M_{\alpha\beta}^j(t, t') a_{j\beta}(t) , \quad (14a)$$

where we have introduced the  $6 \times 6$  matrices

$$W_{\alpha\beta}^j(t, t') = -i \langle\langle A_{j\alpha} | L Q(t) U(t, t') | \rho_{re}(t') A_{j\beta} \rangle\rangle , \quad (14b)$$

$$R_{\alpha\beta}^j(t, t') = \langle\langle A_{j\alpha} | U(t, t') | \rho_{re}(t') A_{j\beta} \rangle\rangle , \quad (14c)$$

and



$$M_{\alpha\beta}^j(t, t') = \int_{\gamma=0}^5 W_{\alpha\gamma}^j(t, t') [R^j(t, t')]_{\gamma\beta}^{-1} \quad (14d)$$

Here  $U(t, t')$  is the time evolution operator

$$U(t, t') = \exp[-iL(t-t')] \quad (14e)$$

Equation (14d) can be recast in matrix notation:

$$M^j(t, t') = W^j(t, t') [R^j(t, t')]^{-1} \quad (14f)$$

Equation (14) describe the time evolution of the 5N dynamical quantities  $a_{j\alpha}$  ( $j = 1, \dots, N$ ;  $\alpha = 1, 2, \dots, 5$ ) and are exact. There are 5N nonlinear coupled differential equations for 5N unknown  $a_{j\alpha}(t)$ . In these equations the time derivative of  $a_{j\alpha}$  at time  $t$  depends on all  $a_{j\beta}$  at the same time. Note that we assume  $A_{j0}$  to be the unit operator, and  $j_0$  normalization requires its expectation value to be independent of time,  $a_{j0} = 1$ . An alternative derivation of Eqs. (14) is also possible [14,16], where the time derivative of  $a_{j\beta}$  at time  $t$  depends on all  $a_{j\beta}$  at previous time  $t' < s < t$ , and the resulting equations are

$$\begin{aligned} \dot{a}_{j\alpha}(t) = & -i \langle \langle A_{j\alpha} | L | \rho_{re}(t) \rangle \rangle \\ & - \int_{t'}^t ds \langle \langle A_{j\alpha} | L M(t, s) Q(s) L | \rho_{re}(t) \rangle \rangle \end{aligned} \quad (15a)$$

where

$$M(t, s) = \exp[-i \int_0^t d\tau Q(\tau) L] \quad (15b)$$

is a time-ordered exponential. Now if we assume that condition (12) holds for all times, then  $Q(t)\rho(t) = 0$ , and we are left with the first term on the right-hand side of both Eqs. (14a) and (15a), which represents a mean field time evolution of the N-particle system. The second terms are the correlation terms and arise from the fact that  $\rho(t) \neq \rho_{re}(t)$  for all times. If we retain up to a given order in the correlation terms in Eqs. (14a) and (15a), then they yield different approximations. However, in this paper we are interested only in the mean field time evolution of the N-particle system, where the time evolution of the expectations of the dynamical quantities,  $A_{j\alpha}$ , are given by

$$\dot{A}_{j\alpha}(t) = 1/N \text{Tr}\{A_{j\alpha} [H, \rho_{re}(t)]\} \quad (16)$$

For our convenience, however, we evaluate explicitly the time evolution of the dynamical quantities

$$\sigma_{j1} = \langle x_j \rangle, \quad \sigma_{j2} = \langle p_j \rangle \quad (17a, b)$$

$$\sigma_{j3} = \langle x_j^2 \rangle - \langle x_j \rangle^2, \quad \sigma_{j4} = \langle p_j^2 \rangle - \langle p_j \rangle^2 \quad (17c, d)$$

$$\sigma_{j5} = [\langle x_j p_j + p_j x_j \rangle - 2\langle x_j \rangle \langle p_j \rangle] \quad (17e)$$

given by [16]

$$\dot{\sigma}_{j1} = \sigma_{j2}/m_j, \quad (18a)$$

$$\dot{\sigma}_{j2} = -\langle V'_j(X) \rangle, \quad (18b)$$

$$\dot{\sigma}_{j3} = \sigma_{j5}/m_j, \quad (18c)$$

$$\dot{\sigma}_{j4} = -\langle V''_j(X) \rangle \sigma_{j5}, \quad (18d)$$

$$\dot{\sigma}_{j5} = 2\left\{\frac{\sigma_{j4}}{m_j} - \langle V''_j(X) \rangle \sigma_{j3}\right\}, \quad (18e)$$

where

$$V'_j(X) = \frac{\partial V}{\partial x_j}, \quad (19a)$$

$$V''_j(X) = \frac{\partial^2 V}{\partial x_j^2}, \quad (19b)$$

$$\langle V'_j(X) \rangle = \int_{-\infty}^{+\infty} dX V'_j(X) \rho_{re}(X, X; t), \quad (19c)$$

$$\rho_{re}(X, X; t) = \prod_{j=1}^N \phi_j(x_j, x_j; t) \quad (19d)$$

$$\phi_j(x_j, x_j; t) = \frac{1}{\sqrt{2\pi\sigma_{j3}}} \exp\left[-\frac{(x_j - \sigma_{j1})^2}{2\sigma_{j3}}\right]. \quad (19e)$$

$\langle V''_j(X) \rangle$  is expressed in a similar way to Eq. (19c) by replacing  $V'_j(X)$  with  $V''_j(X)$ . Equations (18) are the time-dependent self-consistent field<sup>j</sup> (TDSCF) equations. For each particle  $j$  we obtain a closed set of five equations, which show correct self-consistent behavior in any potential and are coupled to each other. The first two equations in (18) express Ehrenfest's Theorem [17], and the third and fourth give a measure of the uncertainty in position and momentum measurement in the system. The fifth equation appears only when we are treating systems in a mixed state. For systems in a pure-state,

$$\sigma_{j5}^2 = (4\sigma_{j3}\sigma_{j4} - \hbar^2). \quad (20)$$

From Eq. (19) we find that for a successful application of the REM, the choice of the form of  $\phi_j$  is crucial. Our particular choice, as described by Eqs. (2) and (19e), is by no means unique. We are motivated by the physical consideration which is the maximum entropy principle [10]. Such choice for  $\phi_j$  connects the present semiclassical procedure with the more general problem of the derivation of REM in nonequilibrium statistical mechanics [18,20].

In the following we show that the choice of the dynamical quantities as described by Eq. (3) produces a Gaussian distribution for each  $\phi_j$  in one-dimensional phase space. We now derive explicitly the phase-space representation  $(q, p)$  for one degree of freedom. The proof holds, however, for any  $N$  since we represent our reduced density function  $\rho_{re}(X, X'; t)$  by a product of  $N$  single-particle density functions  $\phi_j(x_j, x'_j; t)$  (Eq. (1)). We therefore, from now on, choose to drop the subscript  $j$  and replace Eq. (1) by

$$\sigma(x, x', t) \equiv \langle x | \sigma(t) | x' \rangle \quad (21a)$$

with

$$\sigma(t) = \exp\left[\sum_{\alpha=0}^5 \lambda_{\alpha}(t) A_{\alpha}\right] . \quad (21b)$$

As shown in Ref. 16, the Wigner representation [19] of the density operator,  $\sigma(t)$ , may be written in the form

$$\begin{aligned} \sigma_w(q,p;t) = & \frac{1}{\pi} [\alpha\beta - \gamma^2/4]^{\frac{1}{2}} \exp[(\delta^2\beta + \phi^2\alpha - \gamma\delta\phi)/(4\alpha\beta - \gamma^2)] \\ & \times \exp[\alpha q^2 + \beta p^2 + \gamma pq + \delta q + \phi p] \end{aligned}$$

with

$$\iint dq dp \sigma_w(q,p,t) = 1 , \quad (22)$$

and the corresponding coordinate representation is obtained from the transformation

$$\sigma(q+s, q-s; t) = \int_{-\infty}^{\infty} dp \sigma_w(q,p;t) \exp[2ips/\hbar] . \quad (23)$$

Using the substitutions

$$q = (x+x')/2, \quad s = (x-x')/2 \quad (24)$$

in Eq. (23), we obtain

$$\begin{aligned} \sigma(x, x'; t) = & \frac{1}{2\sqrt{\pi\beta}} (\gamma^2 - 4\alpha\beta)^{\frac{1}{2}} \exp[(2\beta\delta - \gamma\phi)^2 / 4\beta(\gamma^2 - 4\alpha\beta)] \\ & \times \exp\left[\frac{1}{4}\left(\alpha - \frac{\gamma^2}{4\beta}\right)(x+x')^2 + \frac{1}{2}\left(\delta - \frac{\gamma\phi}{2\beta}\right)(x+x')\right. \\ & \left. + \frac{1}{4\hbar^2\beta}(x-x')^2 - \frac{i\gamma}{4\beta\hbar}(x^2 - x'^2) - \frac{i\phi}{2\beta\hbar}(x-x')\right] , \end{aligned} \quad (25)$$

with  $\alpha, \beta, \gamma, \delta$  and  $\phi$  being real parameters, which may be expressed in terms of  $\lambda_1, \dots, \lambda_5$ . Equations (22) and (25) accomplish our goal of expressing the maximum entropy distribution [Eq. (21b)] in phase space  $(q,p)$  and in the coordinate representation  $(x,x')$ . However, to obtain the TDSCF set of equations (18), we have used a different form of representation of these distribution functions, which were obtained by expressing Eqs. (22) and (25) in terms of the expectations of the dynamical quantities described by Eq. (17). They are related to the parameters by

$$\sigma_1(t) = \langle x(t) \rangle = (2\beta\delta - \gamma\phi)(\gamma^2 - 4\alpha\beta)^{-1} \quad (26a)$$

$$\sigma_2(t) = \langle p(t) \rangle = (2\alpha\phi - \gamma\delta)(\gamma^2 - 4\alpha\beta)^{-1} \quad (26b)$$

$$\sigma_3(t) = \langle x^2(t) \rangle - \langle x(t) \rangle^2 = 2\beta(\gamma^2 - 4\alpha\beta)^{-1} \quad (26c)$$

$$\sigma_4(t) = \langle p^2(t) \rangle - \langle p(t) \rangle^2 = 2\alpha(\gamma^2 - 4\alpha\beta)^{-1} \quad (26d)$$

$$\sigma_5(t) = \langle xp + px \rangle - 2\langle x \rangle \langle p \rangle = -2\gamma(\gamma^2 - 4\alpha\beta)^{-1} \quad (26e)$$

or

$$\alpha = c\sigma_4, \quad \beta = c\sigma_3, \quad \gamma = -c\sigma_5$$

$$\delta = c(\sigma_2\sigma_6 - 2\sigma_1\sigma_4), \quad \phi = c(\sigma_1\sigma_5 - 2\sigma_2\sigma_3) ,$$

where

$$c = \frac{1}{2}(\gamma^2 - 4\alpha\beta) = \frac{2}{\sigma_5^2 - 4\sigma_3\sigma_4} \quad (27)$$

Expressing the phase-space density function  $\sigma_w(q,p,t)$  of Eq. (22) in terms of the  $\sigma_j(t)$ 's, we have

$$\sigma_w(q,p;t) = \frac{1}{\pi(4\sigma_3\sigma_4 - \sigma_5^2)^{\frac{1}{2}}} \exp\left\{-\frac{2}{4\sigma_3\sigma_4 - \sigma_5^2} [\sigma_4(q - \sigma_1)^2 + \sigma_3(p - \sigma_2)^2 - \sigma_5(q - \sigma_1)(p - \sigma_2)]\right\} \quad (28)$$

and the corresponding coordinate representation (Eq. (25)) becomes

$$\begin{aligned} \sigma(x, x'; t) &= \frac{1}{\sqrt{2\pi\sigma_3}} \exp(-\sigma_1^2/2\sigma_3) \\ &\times \exp\left[-\frac{1}{8\sigma_3}(x+x')^2 + \frac{\sigma_1}{2\sigma_3}(x+x') + \frac{1}{4\hbar^2\sigma_3 c}(x-x')^2\right. \\ &\left.+ \frac{i\sigma_5}{4\sigma_3\hbar}(x^2 - x'^2) - \frac{1}{2\sigma_3\hbar}(\sigma_1\sigma_5 - 2\sigma_2\sigma_3)(x-x')\right] \quad (29) \end{aligned}$$

Thus, the particular choice of the dynamical quantities, as depicted in Eq. (3), generates a Gaussian form for the representation of the corresponding single-particle distribution functions. In the following section we shall show that condition (20) reduces these mixed-state density functions [Eqs. (28) and (29)] to that of pure states. We shall also derive the REM for pure states.

### III. REDUCED EQUATIONS OF MOTION (REM) FOR THE PURE-STATE DENSITY FUNCTION

Using the same projection scheme as in Sec. II, a self-consistent description for the time evolution of the pure-state density function can also be obtained. Following Heller [8], we define the reduced density function for pure states in the coordinate representation as

$$\begin{aligned} \sigma_H(x, x'; t) &= \left(\frac{2\alpha_1}{\pi\hbar}\right)^{\frac{1}{2}} \exp\left[-\frac{\alpha_1}{\hbar} \{(x-x_t)^2 + (x'-x_t)^2\}\right. \\ &\left.+ \frac{1}{\hbar} \alpha_2 \{(x-x_t)^2 - (x'-x_t)^2\} + \frac{1}{\hbar} p_t(x-x')\right] \quad (30) \end{aligned}$$

where the parameters  $\alpha_1$ ,  $\alpha_2$ ,  $x_t$  and  $p_t$  are related to the  $\sigma_j(t)$ 's as follows:

$$\sigma_1(t) = x_t, \quad \sigma_2(t) = p_t \quad (31a, b)$$

$$\sigma_3(t) = \frac{\hbar}{4\alpha_1}, \quad \sigma_4(t) = \frac{\hbar|\alpha|^2}{\alpha_1}, \quad \alpha = i\alpha_1 + \alpha_2 \quad (31c, d)$$

$$\sigma_5(t) = \frac{\hbar\alpha_2}{\alpha_1} = [4\sigma_3(t)\sigma_4(t) - \hbar^2]^{\frac{1}{2}} \quad (31e)$$

Therefore,  $\sigma_H(x, x'; t) = \frac{1}{\sqrt{2\pi\sigma_3}} \exp(-\frac{\sigma_1^2}{2\sigma_3}) \exp[-\frac{1}{4\sigma_3}(x^2 + x'^2) + \frac{\sigma_1}{2\sigma_3}(x+x')]$

$$+ \frac{1\sigma_5}{4\hbar\sigma_3} (x^2 - x'^2) - \frac{1}{2\sigma_3\hbar} (\sigma_1\sigma_5 - 2\sigma_2\sigma_3)(x-x') \quad , \quad (32)$$

and the corresponding phase-space representation is given by

$$\begin{aligned} \rho_{HW}(q,p,t) = & \frac{1}{\pi\hbar} \exp\left[-\frac{2}{\hbar^2} \left\{ \sigma_4(q-\sigma_1)^2 \right. \right. \\ & \left. \left. + \sigma_3(p-\sigma_2)^2 - \sigma_5(q-\sigma_1)(p-\sigma_2) \right\} \right] \quad , \end{aligned} \quad (33)$$

where  $\sigma_5$  is given by (31e), which is the same as condition (20). These pure-state density functions can also be obtained directly from the mixed-state density functions (Eqs. (28) and (29)) using condition (20).

We now assume that the time evolution of the pure-state system is described by the approximate density functions, (32) and (33), for all times. This assumption then allows us to construct the SCF set of equations for the expectations of the corresponding dynamical quantities using Eq. (16). They are

$$\dot{\sigma}_1(t) = \frac{\sigma_2(t)}{m} \quad (34a)$$

$$\dot{\sigma}_2(t) = -\langle V'(x) \rangle \quad (34b)$$

$$\dot{\sigma}_3(t) = \frac{1}{m} (4\sigma_3(t)\sigma_4(t) - \hbar^2)^{\frac{1}{2}} \quad (34c)$$

$$\dot{\sigma}_4(t) = -(4\sigma_3(t)\sigma_4(t) - \hbar^2)^{\frac{1}{2}} \langle V''(x) \rangle \quad . \quad (34d)$$

This is a closed set of four equations which differ from the first four equations in the mixed case [Eqs. (18a) through (18d)] due to the fact that  $\sigma_5$  is no longer an independent variable [Eq. (20)], and for the same reason we do not have any REM for  $\sigma_5$  in the pure case.

The REM of Eq. (34) are obtained from Eq. (16) under the exact potential of the system. These equations, as shown below, are different from those obtained by solving the quantum Liouville equation (5) for pure states under the locally quadratic potential approximation [8]. They are

$$\dot{\sigma}_1(t) = \frac{\sigma_2(t)}{m} \quad (35a)$$

$$\dot{\sigma}_2(t) = -V'(x)|_{x=\sigma_1} \quad (35b)$$

$$\dot{\sigma}_3(t) = (4\sigma_3(t)\sigma_4(t) - \hbar^2)^{\frac{1}{2}}/m \quad (35c)$$

$$\dot{\sigma}_4(t) = -(4\sigma_3(t)\sigma_4(t) - \hbar^2)^{\frac{1}{2}} V''(x)|_{x=\sigma_1} \quad . \quad (35d)$$

Here the first two equations describe the classical motion for a system in a pure state and are not coupled with the other two equations [(35c) and (35d)], which describe the time evolution of the variances (Eqs. (17c), (17d)). Therefore, the present set of equations describe the trajectory of a particle whose position and momentum at time  $t$  are known from the center of the wavepacket. However, the trajectory of a particle is described by the wavepacket [Eqs. (32) and (33)] as a whole, which inevitably has certain spacial extension.

On the other hand, if we look at the SCF set of equations (34), we find that the first two equations (a and b) are coupled with the other two equations. Again, the right-hand side of Eq. (34b) is equal to the average of the force over the whole wavepacket and thus differs from Eq. (35b) due to the fact

$$\langle V'(x) \rangle \neq V'(x)|_{x=\sigma_1} . \quad (36)$$

In Sec. V we shall analyze the relative merits of these approaches by studying the vibrational motion of an arbitrary diatomic molecule on a Morse potential surface. It is important to note here that for the mixed case, even if we start with a minimum uncertainty wavepacket the variances  $\sigma_3$  and  $\sigma_4$  are not constants of motion as the system evolves, which is evident from Eqs. (18). In deriving expressions (32) and (33) we assumed that the N-particle density function may be written as [20]

$$\rho(X, X'; t) = \Psi(X, t) \Psi^*(X', t) , \quad (37)$$

where  $\Psi(X, t)$  is the exact wave function of the N-particle interacting system. We then introduced the approximation

$$\Psi(X, t) = \prod_{j=1}^N \psi_j(x_j, t) , \quad (38)$$

where the  $\psi_j(x_j, t)$ 's are the single-particle wave functions and contain all information about the single-particle systems, including their phase. A reduced description of these single-particle wave functions was first introduced by Heller [8], which in terms of the  $\sigma_i$ 's may be written as

$$\psi(x, t) = (2\pi\sigma_3)^{-1/4} \exp\left\{\left(\frac{1}{4\sigma_3} + \frac{i\sigma_5}{4\hbar\sigma_3}\right)(x-\sigma_1)^2 + \frac{i\sigma_2}{\hbar}(x-\sigma_1) + \frac{i\gamma}{\hbar}\right\} , \quad (39)$$

where for notational convenience we have dropped the subscript j.  $\sigma_5$  is given by condition (20), and  $\gamma$  is the phase-factor. The density function corresponding to this wave function is given by expression (32), which we obtained from the maximum entropy distribution (29) using condition (20). Therefore, if we assume this Gaussian wave function (39) to approximate the exact single particle wave function for all times, the time evolution of this reduced wave function under the exact potential of the system can be obtained by solving the SCF set of REM given by Eqs. (34), along with the equation for the phase factor

$$\dot{\gamma}(t) = -\frac{\hbar}{4m\sigma_3} + \frac{V_2\sigma_3}{2} + \frac{\sigma_2^2}{2m} - V_0 \quad (40)$$

which is obtained from the Schrödinger equation

$$\langle E \rangle = \langle \frac{p^2}{2m} + V(x) \rangle = i\hbar \langle \psi | \dot{\psi} \rangle \quad (41)$$

The quantities  $V_0$ ,  $V_2$  in Eq. (40) are given by

$$V_0 = \langle V \rangle, \quad V_2 = \langle \frac{\partial^2 V}{\partial x^2} \rangle .$$

Heller first evaluated this propagator (39) under the locally-quadratic potential approximation [8].

#### IV. CANONICAL DENSITY FUNCTION FOR A HARMONIC SYSTEM

In this section we show that the TDSCF set of equations (18), which describe the time evolution of any irreversible process under the exact potential of the system by using the reduced density matrix expressions (28) and (29), can be used to describe the time evolution of a harmonic system in thermal equilibrium [15]. When a system is in thermal equilibrium, we have the density matrix satisfying maximum entropy principle as [10]

$$\hat{\rho}_T(t) = \exp(-\beta H) / \text{Tr}[\exp(-\beta H)] , \quad (42)$$

where  $\beta = (kT)^{-1}$  and  $H$  is the Hamiltonian of the system. Under the quadratic potential approximation, where

$$H(q,p) = p^2/2m + \frac{1}{2}m\omega^2 q^2 , \quad (43)$$

a Gaussian form of representation of the density operator (42) can be obtained, which in the coordinate representation  $(x, x')$  is given by

$$\begin{aligned} \sigma_T(x, x'; t) = & \left[ \frac{m\omega \tanh(\beta\hbar\omega/2)}{\pi\hbar} \right]^{\frac{1}{2}} \\ & \times \exp\left\{ \frac{-m\omega}{2\hbar \sinh(\beta\hbar\omega)} [(x^2 + x'^2) \cosh(\beta\hbar\omega) - 2xx'] \right\} . \end{aligned} \quad (44)$$

Expectation values of the dynamical quantities (17), with respect to this density matrix, are

$$\begin{aligned} \sigma_1 = 0 , \quad \sigma_2 = 0 \\ \sigma_3 = \frac{\hbar}{2m\omega} \coth(\frac{1}{2}\beta\hbar\omega) , \quad \sigma_4 = \frac{1}{2}m\omega\hbar \coth(\frac{1}{2}\beta\hbar\omega) , \quad \sigma_5 = 0 , \end{aligned} \quad (45)$$

where for convenience we have dropped the  $j$ -subscript. Now expressing the thermal density function  $\sigma_T$  in terms of the  $\sigma_j(t)$ 's, we obtain

$$\sigma_T(x, x'; t) = \frac{1}{\sqrt{2\pi\sigma_3}} \exp\left\{ -\frac{1}{8\sigma_3}(x+x')^2 - \frac{\sigma_4}{2\hbar^2}(x-x')^2 \right\} , \quad (46)$$

and the corresponding phase-space density function becomes

$$\sigma_{TW}(q, p; t) = \frac{1}{2\pi\sqrt{\sigma_3\sigma_4}} \exp\left[ -\frac{1}{2\sigma_3}q^2 - \frac{1}{2\sigma_4}p^2 \right] . \quad (47)$$

The time evolution of these density functions are found by solving the set of equations (18) with initial conditions given by Eq. (45) and the interaction potential given by expression (43). This is because Eqs. (46) and (47) do not satisfy condition (37). Our development, as described in Sec. II, however, is more general since it can be used for studying the relaxation of a system to thermal equilibrium with a thermal bath under the exact potential of the system.

#### V. VIBRATIONAL MOTION OF AN ARBITRARY DIATOMIC MOLECULE ON A MORSE POTENTIAL SURFACE

In this section we solve the TDSCF set of REM (34) to describe the vibrational motion of a diatomic molecule. We consider a diatomic molecule

with two electronic states, a ground state  $|g\rangle$  and an excited state  $|e\rangle$ . Its Hamiltonian is

$$H = |g\rangle H_g \langle g| + |e\rangle (W_{g,e} + H_e) \langle e| \quad (48)$$

We assume the ground state potential to be harmonic and the excited state potential to be given by a Morse oscillator. We then have

$$H_g = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega_g^2(x-x_g)^2 \quad (49a)$$

$$H_e = \frac{p^2}{2\mu} + W_{g,e} + D_e(1 - e^{-\beta(x-x_e)})^2, \quad (49b)$$

where  $\mu$  is the reduced mass of the molecule,  $\omega$  is the vibrational frequency on the lower potential surface,  $W_{g,e}$  is the excitation energy from lower to the upper surface,  $D_e$  is the equilibrium dissociation energy of the upper potential surface, and  $\beta$  is a constant given by [21]

$$\beta = \left\{ \frac{2\pi^2 c \mu}{D_e h} \right\}^{1/2} \omega_e, \quad (49c)$$

where  $c$  is the velocity of light,  $h$  is Planck's constant, and  $\omega_e$  is the vibrational frequency that the anharmonic oscillator would have classically for an infinitesimal amplitude. For our purposes we assume

$$\begin{aligned} \omega_e &= 4395 \text{ cm}^{-1}, \quad \mu = 0.5 \text{ a.u.}, \quad D_e = 38,310 \text{ cm}^{-1}, \quad D_e = hc\bar{D}_e \\ \beta &= 1.93 \text{ \AA}^{-1}, \quad x_g = 0.504 \text{ \AA}, \quad W_{g,e} = 26,230 \text{ cm}^{-1}, \quad x_e = 0.6325 \text{ \AA} \end{aligned} \quad (50)$$

We consider the molecule initially to be in its ground vibrational state satisfying the minimum uncertainty condition

$$\sigma_3 \sigma_4 = \frac{\hbar^2}{4}, \quad (51)$$

and we set initially  $\sigma_1 = 0.604 \text{ \AA}$  and  $\sigma_2 = 0.0 \text{ gm cm/s}$ . We now assume that at time  $t = 0$  there is a Franck-Condon transition from the ground to the excited potential surface. After this transition the molecule will start executing vibrational motion about the excited state equilibrium position  $X_e$ . To study this vibrational motion, we solve the TDSCF set of REM (34) in dimensionless form, where the dimensionless quantities  $\hat{\sigma}_i$ 's are related to the  $\sigma_i$ 's as

$$\hat{\sigma}_1 = \left\{ \frac{m\omega}{\hbar} \right\}^{1/2} \sigma_1, \quad \hat{\sigma}_2 = \frac{1}{\sqrt{m\hbar\omega}} \sigma_2, \quad \hat{\sigma}_3 = \frac{m\omega}{\hbar} \sigma_3, \quad \hat{\sigma}_4 = \frac{1}{m\hbar\omega} \sigma_4 \quad (52)$$

where  $\omega = 2\pi\omega_e$  with initial conditions (50),  $\hat{\sigma}_3 = 5.0$ ,  $\hat{\sigma}_4 = 0.05$  and with up to 200 time steps on the order of  $\sim 0.3 \times 10^{-15} \text{ s}$ . Variations of  $\hat{\sigma}_1(t)$  and  $\hat{\sigma}_2(t)$  with time are shown in Figs. 1 and 2, respectively. We have used the ordinary differential equation solver technique of Gear [22] to solve the TDSCF set of equations (34). In Fig. 3 we elaborate further on the performance of our SCF approach by tracing the path of  $\sigma_1$  over the excited state potential surface. As evident from Figs. 1 and 2, given the initial  $\sigma_1$  and  $\sigma_2$  on the potential surface, which for the present case is  $\sigma_1 = 0.604 \text{ \AA}$  and  $\sigma_2 = 0.0 \text{ gm cm/s}$ , our TDSCF method describes anharmonic vibrational motion of the diatomic molecule over this surface from  $\sigma_1 = 0.604 \text{ \AA}$  to  $1.08 \text{ \AA}$ .



For the sake of comparison, we also solve in dimensionless form the TDSCF set of REM (35), which describe the variations of  $q_i(t)$ 's with time under the quadratic potential approximation. We use the same set of initial conditions as above. Time variations of  $\hat{q}_1(t)$  and  $\hat{q}_2(t)$  for the present case are shown in Figs. 4 and 5, respectively. In Fig. 3, we trace the path of  $o(t)$  obtained under the quadratic potential approximation using a dashed line to illustrate the performance of Heller's method compared to our TDSCF method.

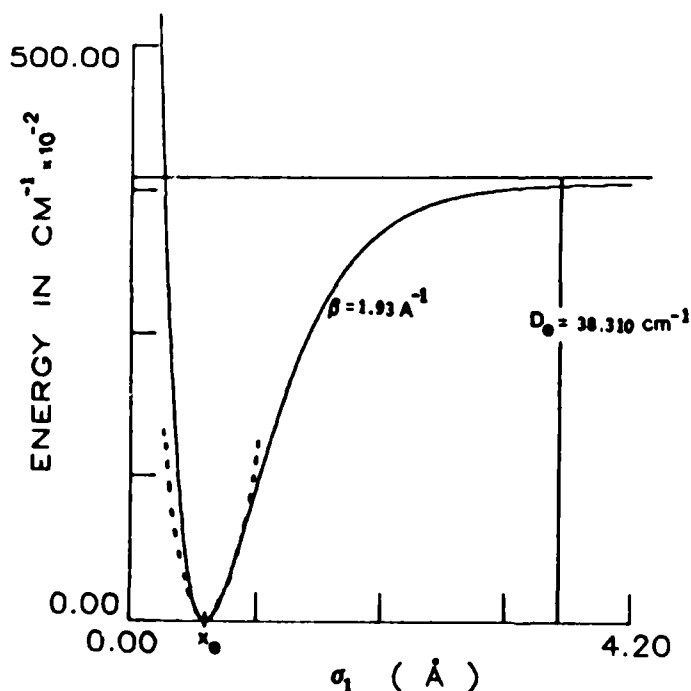
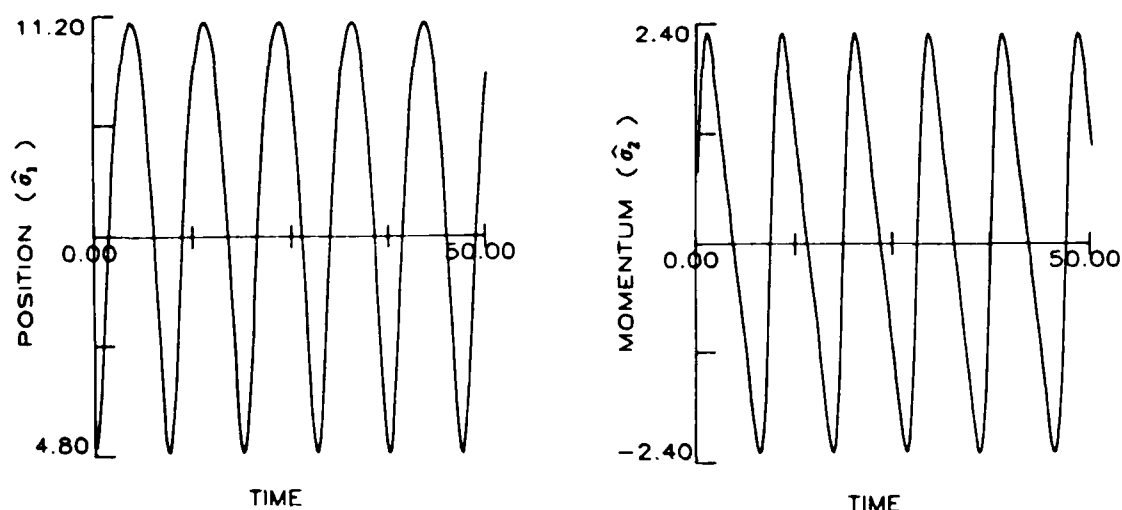


Fig. 1. The dimensionless mean displacement  $\hat{q}_1$  vs time for a Gaussian wavepacket propagated on a Morse potential.

Fig. 2. The dimensionless mean momentum  $\hat{q}_2$  vs time for a Gaussian wavepacket on a Morse potential.

Fig. 3. The Morse (solid line) potential function of an arbitrary diatomic molecule. The dashed line is obtained by considering up to the quadratic terms in  $q_1(t)$  in the Morse function.

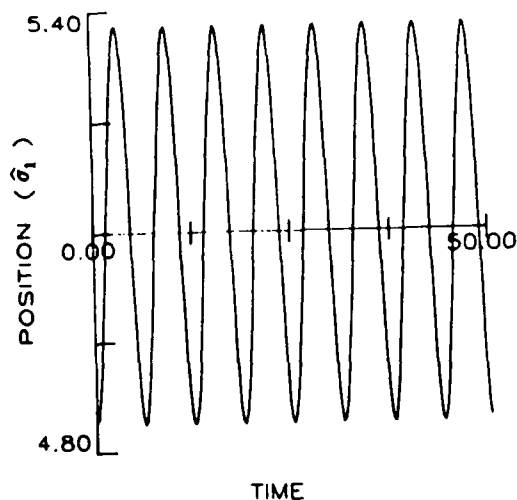


Fig. 4. The dimensionless mean displacement  $\hat{q}_1$  vs time for a Gaussian wavepacket propagated on a locally quadratic form of the Morse potential.

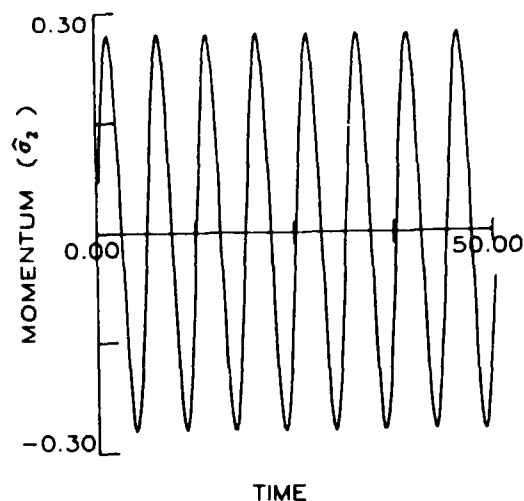


Fig. 5. The dimensionless mean momentum  $\hat{q}_2$  vs time for a Gaussian wavepacket propagated on a locally quadratic form of the Morse potential.

## VI. DISCUSSION

We have described a method for studying the dynamical properties of irreversible statistical systems. Irreversibility is introduced into our system through quantum measurements [20], and this enables us to make use of the maximum entropy-based formulation (MEF). Use of MEF in constructing the reduced density matrix (2) eliminates the necessity of performing tedious thermal averaging [9]. Therefore, the present TDSCF method will be particularly suitable for studying the various dynamical processes in condensed phases. The present development resembles the derivation of thermodynamic theorems from statistical mechanics due to the fact that the construction of the density matrix and the corresponding REM are independent of the specific nature of the Hamiltonian. For this reason, we find that the present method can be used to describe the relaxation of a system to thermal equilibrium with a thermal bath under the exact and the quadratic potential approximations. Under certain conditions (20), the present method can also be used to describe the time evolution of systems in pure states. The derivation of the REM are based on a projection scheme, and the projection operators are defined in terms of the MEF density matrix. The TDSCF set of equations (35) and (40), which describe the time evolution of pure states, have been shown to be quite useful for describing a variety of molecular dynamical processes, including molecular scattering, electronic spectra, dissociation of clusters and thermal desorption from surfaces [9,23]. The present phase space TDSCF method enjoys all these advantages.

In deriving the TDSCF set of equations, we have not had to make the assumption that the exact nonequilibrium statistical density is in some sense approximately equal to the local equilibrium one, and thus the present method is much more general than the local equilibrium formulations. A close look at our TDSCF set of equations (18) shows that they do not contain  $\hbar$ . That is, even though we started our development using the quantum Liouville equation, the time evolution of our MEF-based density functions (28) and (29) is described by a classical TDSCF set of REM. Therefore, the present MEF-based TDSCF method is completely classical. This in turn suggests that the present procedure may be repeated for classical mechanics

by replacing  $L$  in Eq. (5) with the classical Liouville operator. Each single-particle density function  $\phi_j(x_j, x'_j; t)$  should then be replaced by a phase space distribution which is Gaussian in  $x_j$  and  $p_j$  (28). We can then repeat the present procedure to obtain the TDSCF set of REM (18), and hence to confirm their classical nature. Our TDSCF method represents the lowest order of a systematic expansion, (14) and (15), and may therefore be improved by incorporating correlation terms order by order. Inclusion of the correlation terms will cause our REM to contain  $N$ , and hence will depart from the classical picture. Therefore, the correlation terms may be considered as quantum corrections to our classical description [19]. However, for harmonic systems with normal mode  $x_j$ 's, the TDSCF set of REM are exact. An alternative way to improve our TDSCF description would be to include cubic and higher moments to construct each single-particle density matrix  $\phi_j(x_j, x'_j; t)$ . This would then be a departure from the Gaussian picture.

Although the inclusion of the correlation terms, (14) and (15), and the higher moments, (2), would improve our TDSCF description, the product ansatz, (1), for the  $N$ -particle density function implies neglect of exchange effects and an incomplete account of quantum mechanical correlations. This is one of the limitations of our single-particle description of an interacting  $N$ -particle statistical system. Implementation of the exchange effects for equilibrium Bose and Fermi systems are available in the literature [4,24]. Again, the present development is restricted to one dimensional phase space. Extension to the simulation of equilibrium and nonequilibrium statistical systems in three-dimensional phase space will be reported in the future.

#### ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research, the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, and the National Science Foundation under Grant CHE-8620274. The United States Government is authorized to reproduce and redistribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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